



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number:

0 597 393 A1

⑫ EUROPEAN PATENT APPLICATION

⑬ Application number: 93117937.8

⑬ Int. Cl. 5: B01D 53/34, B01D 53/36,
A62D 3/00

⑭ Date of filing: 05.11.93

⑮ Priority: 09.11.92 JP 298806/92
04.12.92 JP 325572/92
14.12.92 JP 332948/92
14.12.92 JP 332949/92
21.12.92 JP 355408/92
21.12.92 JP 355409/92

⑯ Date of publication of application:
18.05.94 Bulletin 94/20

⑰ Designated Contracting States:
DE FR GB

⑰ Applicant: JAPAN PIONICS CO., LTD.
Tokyo Sakurada Bldg. 8F.,
1-3, Nishishinbashi 1-chome
Minato-ku, Tokyo(JP)

⑰ Inventor: Iwata, Keiichi, c/o Japan Pionics
Co., Ltd.
Hiratsuka Factory,
5181, Tamura
Hiratsuka-shi, Kanagawa-ken(JP)
Inventor: Hatakeyama, Toshiya, c/o Japan
Pionics Co., Ltd.
Hiratsuka Factory,
5181, Tamura
Hiratsuka-shi, Kanagawa-ken(JP)

⑰ Representative: Türk, Gille, Hrabal, Leifert
Brucknerstrasse 20
D-40593 Düsseldorf (DE)

⑲ Process for cleaning harmful gas.

⑲ There is disclosed a process for cleaning a gas containing a nitrogen fluoride especially nitrogen trifluoride as the harmful component which comprises bringing the gas into contact with a cleaning agent comprising zirconium or a zirconium-based alloy such as Zr-Fe, Zr-Cu, Zr-Ni, Zr-Al, Zr-Mg, Zr-Ca, Zr-Zn, Zr-La and Zr-Ce to remove the harmful component at 100 to 800 °C, especially 150 to 500 °C. The process is capable of efficiently removing nitrogen fluoride, especially nitrogen trifluoride at a relatively low temperature without generating a harmful byproduct such as nitrogen oxide, and thus exhibits excellent effect on the cleaning of exhaust gas from semiconductor manufacturing process, etc.

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a process for cleaning a harmful gas. More particularly, it pertains to a process for cleaning a nitrogen fluoride such as nitrogen trifluoride which is used or generated in semiconductor manufacturing industry.

10 With the continuous development of semiconductor industry, there has been a steady rise in recent years in the amount of nitrogen trifluoride which is used in the dry etching of silicon and silicon oxide, as a gas for cleaning the chamber of CVD apparatus and the like. Nitrogen trifluoride gas is sparingly soluble in water and rather stable at room temperature with little reactivity with an acid an alkali, but it is highly toxic and exerts adverse influence on human bodies and environment since the maximum permissible concentration thereof in the atmosphere is reported as being 10 ppm. It is therefore, necessary to clean a nitrogen trifluoride-containing gas after being used in semiconductor production process prior to discharge in the 15 atmosphere.

15 In spite of its being stable at ordinary temperature, nitrogen trifluoride generates dinitrogen tetrafluoride, dinitrogen difluoride, dinitrogen hexafluoride, fluorine and the like due to heat, discharge, etc. in etching and cleaning processes, and each of them must be removed as well because of its toxicity stronger than that of nitrogen trifluoride.

20 2. Description of the Related Art

As the method of removing a nitrogen fluoride contained in a mixed gas, there have heretofore been proposed (1) a process wherein the gas is brought into contact with metallic silicon at 100°C or higher (Japanese Patent Application Laid-Open No. 12322/1988), (2) a process wherein the gas is brought into contact with metallic titanium at 200°C or higher (Japanese Patent Publication No. 48571/1988), (3) a process wherein the gas is brought into contact with Si, B, W, Mo, V, Se, Te, Ge or a non-oxide based compound of any of them at 200 to 800°C (Japanese Patent Publication No. 48570/1988), (4) a process wherein the gas is brought into contact with a metal halogenide capable of transhalogenation with nitrogen fluoride (Japanese Patent Publication No. 48569/1988), (5) a process wherein the gas is brought into contact with the oxide of a transition metal such as Fe, Mn or Cu at 250°C or higher (Japanese Patent Application Laid-Open No. 181316/1991), (6) a process wherein the gas is brought into contact with activated carbon at 300 to 600°C (Japanese Patent Application Laid-Open No. 237929/1987), (7) a process wherein the gas is brought into contact with a composition comprising as principal components Ni, Fe, Co or a noble metal such as Pt, Rh and Pd and at least one from alumina and silica at 200°C or higher (Japanese Patent Application Laid-Open No. 27303/1987).

Nevertheless, any of the above-proposed processes is insufficient in gas cleaning capability and besides suffers the disadvantage as described hereunder. A volatile fluoride is produced in the processes (1), (2) & (3), a halogen such as chlorine is formed in the process (4) and a nitrogen oxide is generated in the process (5), each incurring an expense in the treatment of itself. It is necessary in the processes (2) & (3) to heat the reaction system to 300°C or higher in order that the produced fluoride may not cover the surface of the reaction agent and thus hinder the cleaning reaction. The process (6) involves the danger of explosion due to violent reaction at an elevated temperature and the problem of byproducing carbon tetrafluoride that is relatively stable and difficult to remove. In the process (7), a harmful gas is not byproduced but a high temperature is required for attaining sufficient cleaning capability and in the case of nickel (Ni), for example, for the purpose of achieving practical performance, the reaction system needs to be heated to 400°C or higher, that is, much higher than 200°C at which the decomposition activity is insufficient and besides, the surface of the reaction agent is covered with the fluoride with the progress of the reaction, thereby failing to assure sufficient cleaning capability.

50 SUMMARY OF THE INVENTION

Under such circumstances, intensive research and investigation were continued by the present inventors on the development of a process for cleaning nitrogen fluoride with high treatment capacity at a low temperature without producing a harmful gas or a gas having a possibility of causing environmental pollution while solving the disadvantages of the conventional techniques. As a result, it has been found by the present inventors that the nitrogen fluorides can be removed in extremely high efficiency at a relatively low temperature without generating a substance adversely affecting the environment in the exhaust gas

after cleaning treatment by using zirconium or a zirconium-based alloy as the cleaning agent. The present invention has been accomplished on the basis of the above-mentioned finding.

Specifically the present invention provides a process for cleaning a gas containing a nitrogen fluoride as the harmful component which comprises bringing said gas under heating into contact with a cleaning agent comprising zirconium to remove said harmful component and a process for cleaning a gas containing a nitrogen fluoride as the harmful component which comprises bringing said gas under heating into contact with a cleaning agent comprising a zirconium-based alloy to remove said harmful component.

According to the present invention, the nitrogen fluorides including nitrogen trifluoride which is contained in the air, nitrogen, argon and hydrogen and other nitrogen fluoride such as dinitrogen tetrafluoride, dinitrogen difluoride, dinitrogen hexafluoride can efficiently be removed.

DESCRIPTION OF PREFERRED EMBODIMENTS

As the cleaning agent according to the present invention, there is employed zirconium or a zirconium-based alloy. As the zirconium source applicable to the preparation of the cleaning agent according to the present invention, mention may be made of metallic zirconium and sponge zirconium each available on the market, which can be used as such or by crushing them into an appropriate size. The zirconium available on the market sometimes contains hafnium in an amount of about 1 to 5% by weight, but such extent of hafnium content does not exert evil influence on the cleaning capability and is not liable to produce a harmful substance such as a volatile fluoride or nitrogen oxide in the course of cleaning reaction.

The zirconium-based alloy as mentioned above is usually the alloy of zirconium and at least one metallic element selected from the group consisting of iron, copper, nickel, aluminum, magnesium, calcium, zinc, lanthanum, cerium, vanadium, molybdenum, titanium, chromium, tungsten, tantalum, cadmium, yttrium, niobium and tin. The preferable alloy among them includes that of zirconium and at least one element selected from iron, copper, nickel, aluminum, magnesium, calcium, zinc, lanthanum and cerium, since it does not generate a volatile fluoride during the course of reaction with a nitrogen fluoride and is easily available at a relatively low cost.

The nitrogen-fluoride removing function in the present invention is attributable principally to the zirconium component, which function is corroborated by the fact that the powdery substance formed during the cleaning operation as the reaction product of the cleaning agent and a nitrogen fluoride is proved to be mainly zirconium fluoride by the analysis of the substance. Accordingly, the cleaning agent consisting of zirconium as simple substance is characterized by its high cleaning capacity.

In addition, the cleaning capacity per unit weight of the cleaning agent consisting of a zirconium-containing alloy increases with an increase in the content of zirconium in the alloy. However, the alloying metallic component other than zirconium exhibits the effect on lowering the temperature at which a nitrogen fluoride is removed, and such effect is remarkably enhanced by an appropriate content of said component in the alloy. In more detail, the zirconium as simple substance necessitates a temperature of about 300°C for the purpose of attaining practical cleaning capability, whereas the zirconium-containing alloy enables a gas containing a nitrogen fluoride in the same concentration to be treated at a temperature lower than 300°C at the same flow rate. For example, practical cleaning capability is achieved at a lower temperature of 170 to 250°C by appropriately selecting the content the alloying metal other than zirconium at 40% or less by weight.

The content of zirconium in the cleaning agent according to the present invention is not specifically limited, but in the case of zirconium-containing alloy, it is usually 20% or more, desirably 50% or more, more desirably 60% or more by weight with the above-mentioned metallic element as the balance. A content thereof less than 20% by weight results in insufficient capacity of removing nitrogen fluoride and decrease in the effect on lowering the cleaning temperature by alloying and besides causes a fear of byproducing a volatile fluoride depending upon the cleaning conditions.

The zirconium-based alloy can be produced by blending zirconium and the above-mentioned at least one metallic element at a prescribed blending ratio and subsequently alloying the resultant blend through electron beam melting, argon arc melting, high frequency heating melting or resistance heating melting each under vacuum or in an atmosphere of an inert gas or the like method of melting. The alloy thus produced is crushed to 6 to 20 mesh by mechanical crushing by means of a ball mill, jaw crusher, roll mill or the like to be employed as the cleaning agent. Alternatively, it is pulverized to about 100 mesh fine powder, which is made into granule or granulated powder with about 1 to 5 mm in size or molded into pellet to be employed as the cleaning agent. Various zirconium-based alloys available on the market may be employed as it is or after crushing to a suitable size.

The cleaning agent comprising zirconium or the zirconium-based alloy according to the present invention can be used as any of fixed bed, moving bed and fluidized bed. Under ordinary circumstances, the cleaning agent is packed in a cleaning column, and the gas containing a nitrogen fluoride is passed therethrough while being brought into contact with the cleaning agent so that the nitrogen fluoride as the harmful component is removed so as to clean the gas.

5 The temperature at which the gas to be treated is brought into contact with the cleaning agent (cleaning temperature) is usually 100 to 800°C, desirably 150 to 500°C, more desirably 200 to 350°C in case of zirconium, and 150 to 300°C in case of zirconium-based alloy. A temperature lower than 100°C results in deterioration of the capability of removing nitrogen fluoride, whereas that high than 800°C brings about the 10 disadvantages that stainless steel can not be used for the cleaning column, thereby lowering safety and besides increasing heating energy loss.

In the case where an atmospheric component is mixed in the gas to be treated, a high cleaning temperature is liable to cause heat release due to the reaction of the cleaning agent with oxygen and therefore, the cleaning operation is put into practice preferably at 250°C or lower.

15 The pressure during the cleaning operation is usually atmospheric pressure, but can be reduced pressure or raised pressure such as 1 kg/cm² G.

There is no limitation to the flow velocity of the gas to be treated to which the cleaning process according to the present invention is applied, but in general the flow velocity is desirably lowered with increase in the concentration of the nitrogen fluoride contained in the gas to be treated.

20 The cleaning column is designed in accordance with the concentration of the nitrogen fluoride as the harmful gas, the amount and flow rate of the gas to be treated, etc. The space linear velocity (LV) in the column is preferably designed at 20 cm/sec or lower for a relatively low concentration of nitrogen fluoride such as 1000 ppm or less and at 5 cm/sec or lower for the concentration higher than 1000 ppm.

The length of the packed cleaning agent in the cleaning column varies depending on the flow rate of 25 the gas to be treated, the concentration of the harmful gas and the like and can not be unequivocally specified, but is usually 50 to 500 mm, approximately from the practical viewpoint. In general, the length thereof is determined in accordance with the pressure loss through the packed bed, contact efficiency of the gas with the cleaning agent, the concentration of the harmful gas and the like.

30 As mentioned hereinbefore, the reaction during the cleaning operation according to the present invention causes zirconium fluoride to be formed in the form of powder, which is discharged outside the system along with the treated gas or dropped to the bottom of the cleaning column, or allowed to remain in part in the packed zone of the cleaning agent depending on the operational conditions, whereby the pressure loss through the zone is unfavorably increased. Such increase in the pressure loss can be prevented by imparting vibration to the column continuously or intermittently by means of a vibrator or the 35 like fixed to the column to drop the powder down to the bottom of the column. When necessary, a filter for collecting the powder in the treated gas may be installed on the downstream side of the cleaning column.

In summary, according to the process for cleaning a harmful gas of the present invention, nitrogen fluoride such as nitrogen trifluoride contained in a gas can efficiently be removed at a relatively low temperature without producing a harmful byproduct such as a nitrogen oxide. The process, therefore, 40 exhibits excellent effect on the cleaning of exhaust gas from semiconductor manufacturing process or the like.

In the following the present invention will be described in more detail with reference to the non-limitative examples and comparative examples.

45 Example 1

84.9 ml of sponge zirconium that was procured from the market (prepared by screening crushed product to 6 to 32 mesh, with 99.5% purity) was packed in a quartz-made cleaning column having 19 mm inside diameter and 400 mm length. Then, helium (He) gas containing 1% nitrogen trifluoride (NF₃) was 50 passed through the column at a total flow rate of 170 ml/min, that is, a space linear velocity (LV) of 1 cm/sec at 250°C under atmospheric pressure, and the column outlet gas was analyzed for NF₃ by gas chromatography (lower limit of detectable range being 10 ppm). As a result, NF₃ was not detected. Subsequently, the gas was passed through the column for further 3 hours'. As a result, there was not observed break through nor the formation of harmful byproduct such as NO_x.

Example 2

28.3 ml of the sponge zirconium same as that used in Example 1 was packed in a quartz-made cleaning column having 19 mm inside diameter and 400 mm length. Then, He gas containing 1% NF₃ was 5 passed through the column at a total flow rate of 85 ml/min, that is, a space linear velocity (LV) of 0.5 cm/sec at room temperature under atmospheric pressure, and after 20 minutes the column outlet gas was analyzed to determine NF₃ concentration by gas chromatography (lower limit of detectable range being 10 ppm). Subsequently, the gas temperature was raised by increments of 50°C, while the temperature was maintained for 10 minutes at every increment to determine NF₃ concentration in the column outlet gas by 10 gas chromatography and thereby obtain NF₃ decomposition efficiency at each incremental temperature. By plotting the decomposition efficiency thus obtained against the temperature, the lower limit of the temperature at which the NF₃ decomposition efficiency exceeded 90% was obtained by means of interpolation. The result was 280°C.

Thereafter, 8.5 ml of the same sponge zirconium as the cleaning agent was further packed in the 15 column. Subsequently He gas was passed through the column at a total flow rate of 500 ml/min, while the gas temperature was raised to 300°C. Thereafter, He gas containing 2% NF₃ was passed through the column at a total flow rate of 509 ml/min, that is, a LV of 3 cm/sec at 300°C under atmospheric pressure, while the outlet gas was monitored by means of an NF₃ detector available on the market (TG-4100 TA, produced by Bionics Instruments Co., Ltd.) to determine the break through time by regarding the point at 20 which NF₃ concentration in the outlet gas reached 10 ppm as the break through point.

The cleaning capability (throughput of NF₃ (L) per 1L of Zr) was obtained by calculation from the result thus obtained. The result was 711 L/L. In addition in order to check byproduct formation, nitrogen monoxide (NO) and nitrogen dioxide (NO₂) in the exhaust gas were measured prior to the break through by means of the detecting tubes (for separating and analyzing nitrogen oxides, lower limit of detectable range being 1 25 ppm for NO and 0.5 ppm for NO₂, produced by Gastech Corp.). As a result, nitrogen oxide was not detected.

Example 3

28.3 ml of cleaning agent comprising Zr-Fe alloy procured from the market (80% by weight of Zr with the balance Fe) which had been crushed and screened to 10 to 32 mesh was packed in a quartz-made 30 cleaning column having 19 mm inside diameter and 400 mm length. Then He gas containing 1% NF₃ was passed through the column at a total flow rate of 85 ml/min, that is, a space linear velocity (LV) of 0.5 cm/sec at room temperature under atmospheric pressure, and after 20 minutes the column outlet gas was 35 analyzed to determine NF₃ concentration by gas chromatography (lower limit of detectable range being 10 ppm). Subsequently, the gas temperature was raised by increments of 50°C, while the temperature was maintained for 10 minutes at every increment to determine NF₃ concentration in the column outlet gas by gas chromatography and thereby obtain NF₃ decomposition efficiency at each incremental temperature. By plotting the decomposition efficiency thus obtained against the temperature, the lower limit of the 40 temperature at which the NF₃ decomposition efficiency exceeded 90% was obtained by means of interpolation. The result is given in Table 1.

Thereafter, 8.5 mol of the same alloy as the cleaning agent was further packed in the column. Subsequently He gas was passed through the column at a total flow rate of 500 ml/min, while the gas 45 temperature was raised to 200°C. Thereafter, He gas containing 2% NF₃ was passed through the column at a total flow rate of 509 ml/min, that is, a LV of 3 cm/sec under atmospheric pressure, while the outlet gas was monitored by means of an NF₃ detector available on the market (TG-4100 TA, produced by Bionics Instruments Co., Ltd.) to determine the break through time by regarding the point at which NF₃ concentration in the outlet gas reached 10 ppm as the break through point.

The cleaning capability (throughput of NF₃ (L) per 1L of Zr-alloy) was obtained by calculation from the 50 result thus obtained. In addition in order to check byproduct formation, nitrogen monoxide (NO) and nitrogen dioxide (NO₂) in the exhaust gas were measured prior to the break through by means of the detecting tubes (for separating and analyzing nitrogen oxides, lower limit of detectable range being 1 ppm for NO and 0.5 ppm for NO₂, produced by Gastech Corp.). The results are given in Table 2.

Example 4 to 6

Sponge zirconium and reduced iron each procured from the market in a total amount of about 500 g were blended in different compositions (90%, 50% or 40% by weight of Zr and the balance iron) and then

5 melted by electron beam twice repeatedly to afford Zr-Fe alloys, which were crushed in a ball mill and screened to 14 to 20 mesh to prepare various alloys each having a different composition from one another.

Subsequently, the procedure in Example 3 was repeated to carry out cleaning experiment except that each of the above-prepared alloys was used as the cleaning agent and the cleaning temperature was altered, respectively. The results are given in Table 1 and Table 2.

Comparative Example 1

10 The procedure in Example 3 was repeated to carry out cleaning experiment except that there was used as the cleaning agent iron wires procured from the market and cut into a length of 5 to 10 mm. The results are given in table 1 and Table 2.

Table 1

	Alloy composition(wt%)		Lower limit of temperature(°C) attaining≥ 90% decomposition efficiency
	Fe	Zr	
Example 3	20	80	195
Example 4	10	90	195
Example 5	50	50	245
Example 6	60	40	250
Comparative Example 1	100	0	325

Table 2

	Cleaning temperature (°C)	Cleaning capability (L/L)	Nitrogen oxide
Example 3	200	594	ND
Example 4	200	> 100	ND
Example 5	250	> 100	ND
Example 6	280	> 100	ND
Comparative Example 1	300	3	ND
	400	7	ND

Examples 7 to 15

40 sponge zirconium and copper or silver each procured from the market in a total amount of about 500 g were blended in different compositions (40%, 50%, 75% or 90% by weight of Zr and the balance copper or silver) and then melted by electron beam twice repeatedly to afford Zr-Cu or Zr-Ag alloys, which were 45 crushed in a ball mill and screened to 14 to 20 mesh to prepare various alloys each having a different composition. Then, 28.3 ml of each of the alloys was packed in a quartz-made cleaning column having 19 mm inside diameter and 400 mm length. Then, helium (He) gas containing 1% NF₃ was passed through the column at a total flow rate of 85 ml/min, that is, a space linear velocity (LV) of 0.5 cm/sec at room 50 temperature under atmospheric pressure, and after 20 minutes the column outlet gas was analyzed to determine NF₃ concentration by gas chromatography (lower limit of detectable range being 10 ppm). Subsequently, the gas temperature was raised by increments of 100 °C, while the temperature was 55 maintained for 10 minutes at every increment to determine NF₃ concentration in the column outlet gas by gas chromatography and thereby obtain NF₃ decomposition efficiency at each incremental temperature. By plotting the decomposition efficiency thus obtained against the temperature, the lower limit of the temperature at which the NF₃ decomposition efficiency exceeded 90% was obtained by means of interpolation. The result is given in Table 3.

Thereafter, 8.5 ml of each of the alloys as the cleaning agent was further packed in a column. Subsequently He gas was passed through the column at a total flow rate of 500 ml/min, while the gas

temperature was raised to the temperature as shown in Table 2. Thereafter, He gas containing 2% NF₃ was passed through the column at a total flow rate of 509 ml/min, that is, a LV of 3 cm/sec under atmospheric pressure, while the outlet gas was monitored by means of an NF₃ detector available on the market (TG-4100 TA, produced by Bionics Instruments Co., Ltd.) to determine the break through time by regarding the point at which NF₃ concentration in the outlet gas reached 10 ppm as the break through point.

The cleaning capability (throughput of NF₃ (L) per 1L of Zr-alloy) was obtained by calculation from the result thus obtained. In addition in order to check byproduct formation, nitrogen monoxide (NO) and nitrogen dioxide (NO₂) in the exhaust gas were measured prior to the break through by means of the detecting tubes (for separating and analyzing nitrogen oxides, lower limit of detectable range being 1 ppm for NO and 0.5 ppm for NO₂, produced by Gastech Corp.). The result are given in Table 4.

Comparative Examples 2 to 3

The procedure in Example 3 was repeated to carry out cleaning experiment except that there were used as the copper source, copper wires procured from the market and cut into a length of 5 to 10 mm. The results are given in Table 3 and Table 4.

Table 3

	Alloy composition(wt%)			Lower limit of temperature(°C) attaining≥ 90% decomposition efficiency
	Zr	Cu	Ag	
Example 7	40	60	0	235
Example 8	50	50	0	235
Example 9	75	25	0	220
Example 10	90	10	0	225
Example 11	40	0	60	260
Example 12	50	0	50	255
Example 13	75	0	25	235
Example 14	90	0	10	250
Example 15	75	15	10	225
Comparative Example 2	0	100	0	335
Comparative Example 3	0	0	100	430

Table 4

	Cleaning temperature (°C)	Cleaning capability (L/L)	Nitrogen oxide
Example 7	280	> 100	ND
Example 8	250	> 100	ND
Example 9	230	568	ND
Example 10	230	> 100	ND
Example 11	280	> 100	ND
Example 12	280	> 100	ND
Example 13	250	> 100	ND
Example 14	260	> 100	ND
Example 15	250	> 100	ND
Comparative Example 2	350	19	ND
Comparative Example 3	500	8	ND

Examples 16 to 29

Sponge zirconium and nickel, cobalt or manganese each procured from the market in a total amount of about 500 g were blended in different compositions (40%, 50%, 75% or 90% by weight of Zr and the

balance Ni, Co or Mn) and then melted by electron beam twice repeatedly to afford Zr-Ni, Zr-Co or Zr-Mn alloys, which were crushed in a ball mill and screened to 14 to 20 mesh to prepare various alloys as cleaning agent each having a different composition from one another. Then 28.3 ml of each of the alloys was packed in a quartz-made cleaning column having 19 mm inside diameter and 400 mm length. Each of the Zr-alloys as the cleaning agent was tested in the same manner as in Example 7 to determine the temperature attaining 90% decomposition efficiency, cleaning capability and nitrogen oxide concentration. The results are given in Table 5.

Comparative Examples 4 to 6

The procedure in Example 16 was repeated to carry out cleaning experiment except that there was used as the cleaning agent, Ni, Co or Mn procured from the market and screened to 6 to 32 mesh. The results are given in Table 5 and Table 6.

Table 5

	Alloy composition(wt%)				Lower limit of temperature(° C) attaining \geq 90% decomposition efficiency
	Zr	Ni	Co	Mn	
Example 16	40	60	0	0	240
Example 17	50	50	0	0	220
Example 18	75	25	0	0	205
Example 19	90	10	0	0	205
Example 20	40	0	60	0	260
Example 21	50	0	50	0	240
Example 22	75	0	25	0	225
Example 23	90	0	10	0	225
Example 24	40	0	0	60	265
Example 25	50	0	0	50	245
Example 26	75	0	0	25	245
Example 27	90	0	0	10	240
Example 28	75	15	10	0	210
Example 29	90	5	0	5	215
Comparative Example 4	0	100	0	0	290
Comparative Example 5	0	0	100	0	315
Comparative Example 6	0	0	0	100	340

40

45

50

55

Table 6

	Cleaning temperature (°C)	Cleaning capability (L/L)	Nitrogen oxide
5	Example 16	280	> 100
	Example 17	250	> 100
	Example 18	210	504
	Example 19	210	> 100
10	Example 20	280	> 100
	Example 21	250	> 100
	Example 22	240	> 100
	Example 23	240	> 100
15	Example 24	280	> 100
	Example 25	280	> 100
	Example 26	250	> 100
	Example 27	250	> 100
20	Example 28	210	> 100
	Example 29	215	> 100
	Comparative Example 4	300	17
	Comparative Example 5	330	10
25	Comparative Example 6	350	11

Examples 30 to 51

Sponge zirconium and magnesium, calcium, zinc, aluminum, lanthanum or cerium each procured from the market in a total amount of about 500g were blended in different compositions (40%, 50%, 75% or 90% by weight of Zr and the balance Mg, Ca, Zn, Al, La or Ce) and then melted by electron beam twice repeatedly to afford Zr-Mg, Zr-Ca, Zr-Zn, Zr-Al or Zr-Ce alloys, which were crushed in a ball mill and screened to 14 to 20 mesh to prepare various alloys as cleaning agent each having a different composition from one another. Each of the cleaning agents was tested in the same manner as in Example 7 to determine the temperature attaining 90% decomposition efficiency, cleaning capability and nitrogen oxide concentration. The results are given in Table 7 and Table 8.

Comparative Examples 7 to 11

The procedure in Example 30 was repeated to carry out cleaning experiment except that there was used as the cleaning agent, sand magnesium, granular calcium, granular zinc (1 to 2 mm size), granular aluminum (2 to 3 mm size) or granular cerium (1 to 2 mm size). The results are given in Table 7 and Table 8.

45

50

55

Table 7

		Alloy composition(wt%)		Lower limit of temperature(°C) attaining $\geq 90\%$ decomposition efficiency	
		Zr	other metal		
5	Example 30	40	Mg	60	225
	Example 31	50	Mg	50	225
	Example 32	75	Mg	25	190
	Example 33	90	Mg	10	195
10	Example 34	40	Ca	60	230
	Example 35	50	Ca	50	230
	Example 36	75	Ca	25	200
	Example 37	90	Ca	10	210
15	Example 38	40	Zn	60	245
	Example 39	50	Zn	50	215
	Example 40	75	Zn	25	205
20	Example 41	90	Zn	10	200
	Example 42	40	Al	60	240
	Example 43	50	Al	50	240
	Example 44	75	Al	25	215
25	Example 45	90	Al	10	210
	Example 46	40	La	60	245
	Example 47	50	La	50	240
	Example 48	75	La	25	230
30	Example 49	90	La	10	240
	Example 50	40	Ce	60	235
	Example 51	50	Ce	50	245
	Example 52	75	Ce	25	215
35	Example 53	90	Ce	10	225
	Example 54	75	Mg 15	Al 10	195
	Example 55	90	Mg 5	Zn 5	195
40	Comparative Example 7	0	Mg	100	270
	Comparative Example 8	0	Ca	100	280
	Comparative Example 9	0	Zn	100	340
45	Comparative Example 10	0	Al	100	465
	Comparative Example 11	0	La	100	320
50	Comparative Example 12	0	Ce	100	310

Table 8

	Cleaning temperature (°C)	Cleaning capability (L/L)	Nitrogen oxide
5	Example 30	250	> 100
	Example 31	250	> 100
	Example 32	200	404
	Example 33	200	> 100
10	Example 34	250	> 100
	Example 35	250	> 100
	Example 36	210	389
	Example 37	220	> 100
15	Example 38	280	> 100
	Example 39	250	> 100
	Example 40	230	381
20	Example 41	230	> 100
	Example 42	280	> 100
	Example 43	250	> 100
	Example 44	230	495
25	Example 45	230	> 100
	Example 46	260	> 100
	Example 47	260	> 100
	Example 48	250	406
30	Example 49	260	> 100
	Example 50	250	> 100
	Example 51	250	> 100
	Example 52	230	> 100
35	Example 53	230	> 100
	Example 54	210	> 100
	Example 55	210	> 100
40	Comparative Example 7	300	16
	Comparative Example 8	300	11
	Comparative Example 9	400	25
45	Comparative Example 10	500	9
	Comparative Example 11	350	12
50	Comparative Example 12	350	19

Examples 56 to 88

55

Sponge zirconium and vanadium, molybdenum, titanium, chromium, tungsten, tantalum, niobium or tin each procured from the market in a total amount of about 500 g were blended in different compositions (40%, 50%, 70% or 90% by weight of Zr and the balance V, Mo, Ti, Cr, W, Ta or Nb or 50%, 70% or 90%

by weight of Zr and the balance Sn) and then melted by electron beam twice repeatedly to afford Zr-V, Zr-Mo, Zr-Ti, Zr-Cr, Zr-W, Zr-Ta, Zr-Nb or Zr-Sn alloys, which were crushed in a ball mill and screened to 14 to 20 mesh to prepare various alloys as cleaning agent each having a different composition from one another. Then 28.3 ml of each of the alloys was packed in a quartz-made cleaning column having 19 mm inside diameter and 400 mm length. Each of the Zr-alloys as the cleaning agent was tested in the same manner as in Example 7 to determine the temperature attaining 90% decomposition efficiency, cleaning capability and nitrogen oxide concentration. The results are given in Table 10.

Comparative Examples 13 to 20

The procedure in Example 56 was repeated to carry out cleaning experiment except that there was used as the cleaning agent, V, Mo, Ti, Cr, W, Ta, Nb or Sn (1 to 2 mm in granule size) procured from the market. The results are given in Table 9 and Table 10, but the cleaning capability of Sn granule was not measured because of its failure to achieve 90% decomposition efficiency.

Table 9-1

	Alloy composition(wt%)			Lower limit of temperature(° C) attaining \geq 90% decomposition efficiency
	Zr	other metal		
Example 56	40	V	60	235
Example 57	50	V	50	205
Example 58	70	V	30	170
Example 59	90	V	10	175
Example 60	40	Mo	60	250
Example 61	50	Mo	50	190
Example 62	70	Mo	30	180
Example 63	90	Mo	10	180
Example 64	40	Ti	60	205
Example 65	50	Ti	50	195
Example 66	70	Ti	30	165
Example 67	90	Ti	10	170
Example 68	40	Cr	60	230
Example 69	50	Cr	50	235
Example 70	70	Cr	30	200
Example 71	90	Cr	10	205
Example 72	40	W	60	195
Example 73	50	W	50	185
Example 74	70	W	30	180
Example 75	90	W	10	185
Example 76	40	Ta	60	185
Example 77	50	Ta	50	180
Example 78	70	Ta	30	175
Example 79	90	Ta	10	190
Example 80	40	Nb	60	225

Table 9-2

	Alloy composition(wt%)			Lower limit of temperature(° C) attaining≥ 90% decomposition efficiency
	Zr	other metal		
Example 81	50	Nb	50	195
Example 82	70	Nb	30	175
Example 83	90	Nb	10	185
Example 84	50	Sn	50	200
Example 85	70	Sn	30	195
Example 86	90	Sn	10	200
Example 87	70	V 15	Ti 15	160
Example 88	90	V 5	Mo 5	175
Comparative Example 13	0	V	100	415
Comparative Example 14	0	Mo	100	395
Comparative Example 15	0	Ti	100	285
Comparative Example 16	0	Cr	100	435
Comparative Example 17	0	W	100	450
Comparative Example 18	0	Ta	100	425
Comparative Example 19	0	Nb	100	430
Comparative Example 20	0	Sn	100	-

Table 10-1

	Cleaning temperature (° C)	Cleaning capability (L/L)	Nitrogen oxide
Example 56	250	> 100	ND
Example 57	220	> 100	ND
Example 58	180	> 100	ND
Example 59	180	> 100	ND
Example 60	280	> 100	ND
Example 61	200	> 100	ND
Example 62	190	> 100	ND
Example 63	190	> 100	ND
Example 64	220	> 100	ND
Example 65	200	> 100	ND
Example 66	180	> 100	ND
Example 67	180	> 100	ND
Example 68	250	> 100	ND
Example 69	250	> 100	ND
Example 70	230	> 100	ND
Example 71	230	> 100	ND
Example 72	220	> 100	ND
Example 73	200	> 100	ND
Example 74	190	> 100	ND
Example 75	190	> 100	ND
Example 76	210	> 100	ND
Example 77	200	> 100	ND
Example 78	200	> 100	ND
Example 79	200	> 100	ND
Example 80	250	> 100	ND

Table 10-2

	Cleaning temperature (°C)	Cleaning capability (L/L)	Nitrogen oxide
5	Example 81	210	> 100
	Example 82	190	> 100
	Example 83	190	> 100
10	Example 84	220	> 100
	Example 85	220	> 100
	Example 86	220	> 100
	Example 87	180	> 100
	Example 88	190	> 100
15	Comparative Example 13	450	23
	Comparative Example 14	450	28
	Comparative Example 15	300	41
	Comparative Example 16	450	10
	Comparative Example 17	470	21
	Comparative Example 18	450	22
20	Comparative Example 19	450	34
	Comparative Example 20	-	ND

Claims

1. A process for cleaning a gas containing a nitrogen fluoride as the harmful component which comprises bringing said gas under heating into contact with a cleaning agent comprising zirconium to remove said harmful component.
2. A process for cleaning a gas containing a nitrogen fluoride as the harmful component which comprises bringing said gas under heating into contact with a cleaning agent comprising a zirconium-based alloy to remove said harmful component.
3. The process according to Claim 2 wherein the zirconium-based alloy is an alloy of zirconium and at least one metallic element selected from the group consisting of iron, copper, nickel, aluminum, magnesium, calcium, zinc, lanthanum, cerium, vanadium, molybdenum, titanium, chromium, tungsten, tantalum, cadmium, yttrium, niobium and tin.
4. The process according to Claim 3 wherein the zirconium-based alloy is an alloy of zirconium and at least one metallic element selected from the group consisting of iron, copper, nickel, aluminum, magnesium, calcium, zinc, lanthanum and cerium.
5. The process according to Claim 2 wherein the content of zirconium in said zirconium-based alloy is at least 20% by weight.
6. The process according to Claim 5 wherein the content of zirconium in said zirconium-based alloy is at least 50% by weight.
7. The process according to Claim 1 wherein the nitrogen fluoride as the harmful component comprises nitrogen trifluoride or comprises nitrogen trifluoride and at least one member selected from the group consisting of dinitrogen tetrafluoride, dinitrogen difluoride and dinitrogen hexafluoride.
8. The process according to Claim 2 wherein the nitrogen fluoride as the harmful component comprises nitrogen trifluoride or comprises nitrogen trifluoride and at least one member selected from the group consisting of nitrogen trifluoride, dinitrogen tetrafluoride, dinitrogen difluoride and dinitrogen hexafluoride.
9. The process according to Claim 1 wherein the gas is brought into contact with the cleaning agent at a temperature in the range of 100 to 800 °C.

10. The process according to Claim 2 wherein the gas is brought into contact with the cleaning agent at a temperature in the range of 100 to 800 °C.
11. The process according to Claim 2 wherein the content of zirconium in said zirconium-based alloy is at least 60% by weight and the gas is brought into contact with the cleaning agent at a temperature in the range of 170 to 250 °C.
5

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 7937

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	US-A-4 339 309 (UNITED STATES DEPARTMENT OF ENERGY) * claims 1,3 *	1	B01D53/34 B01D53/36 A62D3/00
A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 431 (C-983)9 September 1992 & JP-A-04 149 010 (JAPAN PIONICS) 22 May 1992 * abstract *	1,2	
A	EP-A-0 365 490 (SAES GETTERS) * claims *	1-6	
A	EP-A-0 384 802 (L'AIR LIQUIDE) * claims 1,6 *	1	
A	EP-A-0 431 351 (MAN TECHNOLOGIE AG) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			B01D A62D
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search		Examiner
THE HAGUE	8 February 1994		Bogaerts, M
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>			
<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			